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Electron in a One-Dimensional Well

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An Electron in a One-Dimensional Well

References

Thirty Years That Shook Physics: the story of quantum theory, G. Gamow (Doubleday, 1966) (Olin QC174.1 G3); (Dover, 1985) (Physics QC174.12 G35 1985).
Quantum Mechanics, A. S. Davydov, §25 (Chem QC174.1 D3713 1976).
Quantum Mechanics, L. I. Schiff, §9 (Chem QC174.1 S34 1955).

Energy Quantization

1. In order to explain the spectrum of blackbody radiation M. Planck (1901) added to classical physics the rules

- the energy of an electromagnetic (EM) field cannot be just *any* value; it must be an integral multiple of a fundamental unit.
- the fundamental unit is $\propto$ the frequency

$$\Delta E = h\nu.$$

Hence we speak of the *photon* $\equiv$ 1 quantum of EM energy. Einstein (1904) showed that this energy quantization, which Planck had only used in calculating an ensemble average, could be used at an elementary particle level to explain the photoelectric effect.

A. H. Compton (1923) showed that in x-ray – electron scattering experiments the photon carried a momentum

$$p_{photon} = \frac{h\nu}{c} = \frac{h}{\lambda}.$$

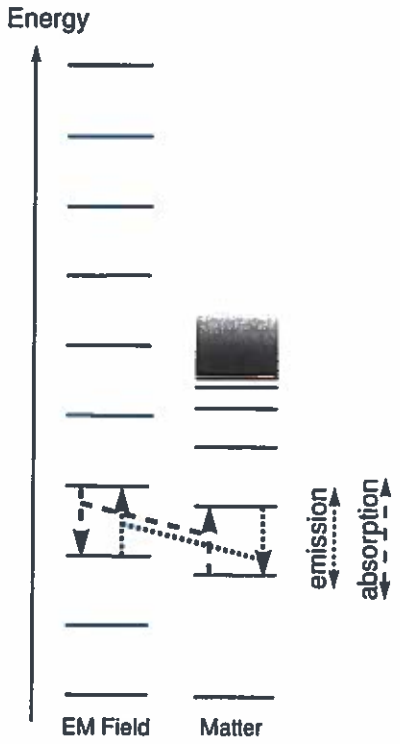
2. To explain the spectrum of the hydrogen atom, N. Bohr (1913) gave a *quantization rule* for electronic motion which identified *energy levels* in that system.

3. Hence this picture: The *allowed* energies of the EM field and matter can be shown in a *level diagram* and spectroscopy becomes the study of *transitions* betwen allowed energies.

Note these general features:

- Every system has a *ground state*. A vacuum is the ground state of the EM field.
- For matter
  - level spacing generally gets smaller as energy rises,
  - there is a continuum limit: above a threshold energy an electron becomes free.
- Spectroscopy ~ energy exchange:

  EM field ⇌ matter.



Wave Mechanics

The classical EM theory of Maxwell treated light like a wave. Planck and Einstein added a particle character. L. deBroglie (1923) reversed the argument:

$$p_{photon} = \frac{h}{\lambda} \quad \longrightarrow \quad \lambda = \frac{h}{p} \sim \text{the deBroglie wavelength}$$

associated with a particle of momentum p. Davisson and Germer (1927) and G. P. Thomson (1928) showed that a beam of electrons scattered by a thin gold foil showed the sort of interference rings expected for waves of wavelength λ.

P. Debye, on hearing a student seminar on deBroglie's wave hypothesis, asked "if there are waves, what is the 'wave equation'?" E. Schrödinger (1926), in the audience, went off and constructed one: If

$$\Psi(x,t) = Ae^{2\pi i\left(\frac{x}{\lambda}-\nu t\right)}$$

then

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) = \frac{p^2}{2m}\Psi(x,t) = [\mathcal{E} - V(x)]\Psi(x,t)$$

follows from deBroglie's hypothesis ($\hbar = h/2\pi$) and

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = h\nu\Psi(x,t) = \mathcal{E}\Psi(x,t) \tag{1}$$

follows from Einstein's hypothesis. Eliminating $\mathcal{E}$ gives

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t).$$

Note that

- this is a *dynamical equation*. It tells how Ψ evolves in time.
- it is not obvious what Ψ represents. The simplest rule is

$$\int_a^b |\Psi(x,t)|^2\,dx = \text{Prob}[a \le x \le b] \text{ at time } t.$$

- the "derivation" is heuristic. A fundamental law can't be "derived."

What are the allowed energies?

A function of the form

$$\Psi(x,t) = e^{-iEt/\hbar}\psi(x)$$

will be a solution to (1) with $\mathcal{E} = E$ if

$$-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\psi(x). \tag{2}$$

If we add the boundary conditions

$$\psi(x) \underset{x\to\pm\infty}{\longrightarrow} 0 \tag{3}$$

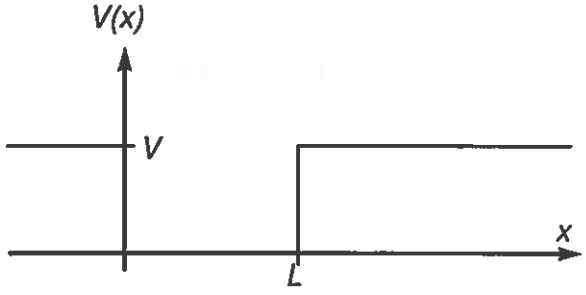
we find that there are solutions to (2) and (3) only for *some* E values, $E_0, E_1, \ldots$. That is, E is quantized!

$$\begin{cases} E_n \sim \text{energy eigenvalues} \\ \psi_n(x) \sim \text{energy eigenstates} \end{cases}$$

$V(x)$ characterizes the system. Different $V(x)$'s give different sets of eigenvalues/eigenstates.

The bound states in a finite well

Consider this potential in one-dimension:



characterized by two parameters, V, L.

This is *qualitatively* like an electron in an atom!

An electron with energy $E > V$ is unbound. Consider $0 \le E \le V$.

$$\psi''(x) + \frac{2m(E - V(x))}{\hbar^2}\psi(x) = 0$$

with

$$\frac{2m(E - V(x))}{\hbar^2} = \begin{cases} < 0, & x < 0, \\ > 0, & 0 \le x \le L, \\ < 0, & x > L. \end{cases}$$

If we set

$$k^2 = \frac{2mE}{\hbar^2} > 0; \qquad \ell^2 = \frac{2m(V - E)}{\hbar^2} > 0.$$

then

$$\begin{aligned} \psi''(x) - \ell^2\psi(x) &= 0; & x < 0, \\ \psi''(x) + k^2\psi(x) &= 0; & 0 \le x \le L, \\ \psi''(x) - \ell^2\psi(x) &= 0; & x > L. \end{aligned}$$

The general solution to $\psi''(x) - \ell^2\psi(x) = 0$ is

$$\psi(x) = Ae^{\ell x} + De^{-\ell x}$$

with A, D arbitrary. The boundary conditions for $x < 0$ ($x > L$) require $D = 0$ ($A = 0$). Inside the well the general solution is

$$\psi(x) = c_1 e^{ikx} + c_2 e^{-ikx} = B \sin kx + C \cos kx$$

Thus

$$\psi(x) = \begin{cases} Ae^{\ell x}; & x \le 0, \\ B \sin kx + C \cos kx; & 0 \le x \le L, \\ De^{-\ell x}; & x > L. \end{cases}$$

There remain 5 unknowns: The coefficients A, B, C, D and the energy E.

Although the solution $\psi(x)$ is prescribed in pieces, the pieces must be connected. $\psi(x)$ is *continuous* $\Rightarrow$

$$\begin{aligned} A &= C, \\ B\sin kL + C\cos kL &= De^{-\ell L}, \end{aligned}$$

and $\psi'(x)$ is continuous $\Rightarrow$

$$\begin{aligned} \ell A &= kB, \\ kB\cos kL - kC\sin kL &= -\ell De^{-\ell L}. \end{aligned}$$

In matrix form,

$$\begin{bmatrix} 1 & 0 & -1 & 0 \\ 0 & \sin kL & \cos kL & -e^{-\ell L} \\ \ell & -k & 0 & 0 \\ 0 & k\cos kL & -k\sin kL & \ell e^{-\ell L} \end{bmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = 0$$

While $A = B = C = D = 0$ (i.e., $\psi(x) \equiv 0$) is always a solution, a non-trivial solution will only be present if

$$0 = \det \begin{vmatrix} 1 & 0 & -1 & 0 \\ 0 & \sin kL & \cos kL & -e^{-\ell L} \\ \ell & -k & 0 & 0 \\ 0 & k\cos kL & -k\sin kL & \ell e^{-\ell L} \end{vmatrix}$$

$$= e^{-\ell L}[2kl\cos kL + (\ell^2 - k^2)\sin kL]$$

Since k and ℓ vary with E, only certain E values will make this zero. These are the allowed (bound state) energies.

If E is an allowed value, the set of four matching relations for A, B, C, D is reduced to three linearly independent equations. We can determine A/D, B/D, C/D, but no more.

A complete solution comes from adding a 5^{th} requirement:

$$\psi(x) \text{ is normalized} \iff \int_{-\infty}^{\infty} |\psi(x)|^2\, dx = 1.$$

Explicitly,

$$\begin{aligned} 1 &= \int_{-\infty}^{0} A^2 e^{2\ell x}\, dx + \int_0^L [B\sin kx + C\cos kx]^2\, dx + \int_L^{\infty} D^2 e^{-2\ell x}\, dx \\ &= \frac{A^2 + D^2 e^{-2\ell L}}{2\ell} + \frac{(B^2 + C^2)kL + 2BC\sin^2 kL}{2k} \end{aligned}$$

For each allowed E this gives a different relation and hence different values for A, B, C, D.

The energy levels with $0 \leq E \leq V$ are fixed by

$$\begin{cases} 2k\ell \cos kL = (k^2 - \ell^2) \sin kL, \\ \hbar k = \sqrt{2mE}, \\ \hbar \ell = \sqrt{2m(V-E)}. \end{cases}$$

There is no *explicit* formula for the E values which satisfy these equations. We will thus determine the solutions *numerically*. Numerical work requires some choice of units. In the following analysis (this is in the *Mathematica* file, "Electron in Well.nb") the bound states are determined for a well of width 8 and depth 1 in *atomic units*.

The Mathematica File

The wave function $f(x)$ assumes three different forms in the three domains:

$$f(x) = \begin{cases} f1[x], & \text{for } x < 0 \\ f2[x], & \text{for } 0 < x < L \\ f3[x], & \text{for } < x \end{cases}$$

In[1]:=

```
f1[x_]:=A E^(l x)
f2[x_]:=B Sin[k x] + C Cos[k x]
f3[x_]:=D E^(-l x)
```

The boundary conditions require that the following four expressions be zero:

In[4]:=

```
ex[1]=f1[0]-f2[0]
ex[2]=f1'[0]-f2'[0]
ex[3]=f2[L]-f3[L]
ex[4]=f2'[L]-f3'[L]
```

Out[4]:=

$A - C$

Out[5]:=

$-(B * k) + A * l$

Out[6]:=

$-(D/E^{l*L}) + C * Cos[k * L] + B * Sin[k * L]$

Out[7]:=

$$(D * l)/E^{l*L} + B * k * Cos[k * L] - C * k * Sin[k * L]$$

A non-null solution for A, B, C, D requires that these equations be linearly dependent. This occurs when the determinant of

In[8]:=

```
m=Table[{D[ex[i],A],D[ex[i],B],D[ex[i],C],D[ex[i],D]},{i,1,4}];
```

is zero.

In[9]:=

```
MatrixForm[m]
```

Out[9]:=

$$m = \begin{bmatrix} 1 & 0 & -1 & 0 \\ l & -k & 0 & 0 \\ 0 & Sin[k * L] & Cos[k * L] & -E^{-l*L} \\ 0 & k * Cos[k * L] & -(k * Sin[k * L]) & E^{-l*L} \end{bmatrix}$$

In[10]:=

```
Det[m]
```

Out[10]:=

$$\frac{-2 * k * l * Cos[k * L]}{E^{l*L}} + \frac{k^2 * Sin[k * L]}{E^{l*L}} - \frac{l^2 * Sin[k * L]}{E^{l*L}}$$

In[11]:=

```
secularEqn=Simplify[%*E^lL]
```

Out[11]:=

$$-2 * k * l * Cos[k * L] + k^2 * Sin[k * L] - l^2 * Sin[k * L]$$

As a numerical example, let us take

In[12]:=

```
numbs={L -> 8,k -> Sqrt[2 e],l -> Sqrt[2-2e]}
```

Out[12]:=

$$L \to 8, k \to \sqrt{2 * e}, l \to \sqrt{(2 - 2 * e)}$$

In[13]:=

```
secularEqn/.numbs
```

Out[13]:=

$$-2*\sqrt{2}*\sqrt{(2-2*e)}*\sqrt{e}*Cos[8*\sqrt{2*e}]-(2-2*e)*Sin[8*\sqrt{2*e}]+2*e*Sin[8*\sqrt{2*e}]$$

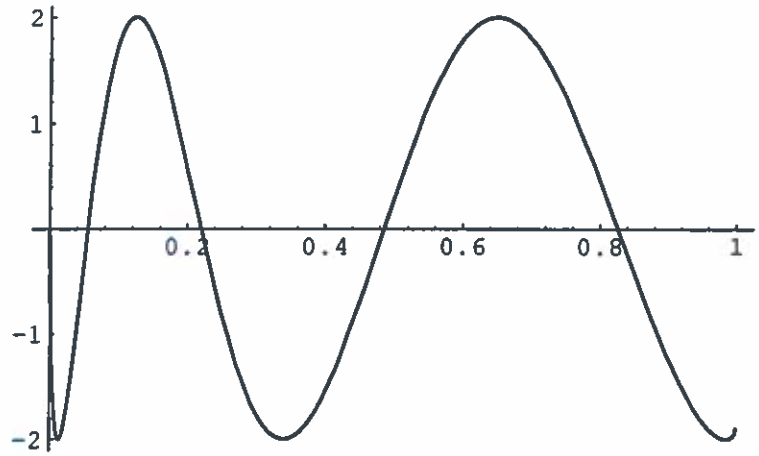
The energy eigenvalues are the values of e which make this expression zero. We can find these by seting a function equal to this expression and then looking for the zeros of the function. From a plot we can get a first order idea of where the zeros are. We can then get an accurate identification by using a 'root finding' algorithm.

In[14]:=

```
g[e_]:=-2*2^(1/2)*(2 - 2*e)^(1/2)*e^(1/2)*Cos[8*2^(1/2)*e^(1/2)]-
    (2 - 2*e)*Sin[8*2^(1/2)*e^(1/2)] + 2*e*Sin[8*2^(1/2)*e^(1/2)]
```

In[15]:=

```
Plot[g[e],{e,0,1}]
```



Out[15]:=

- Graphics -

In[16]:=

```
e1=e/.FindRoot[g[e],{e,.1}]
```

Out[16]:=

0.0555218

In[17]:=

```
e2=e/.FindRoot[g[e],{e,.2}]
```

Out[17]:=

0.220012

In[18]:=

```
e3=e/.FindRoot[g[e],{e,.5}]
```

Out[18]:=

0.485484

In[19]:=

```
e4=e/.FindRoot[g[e],{e,.8}]
```

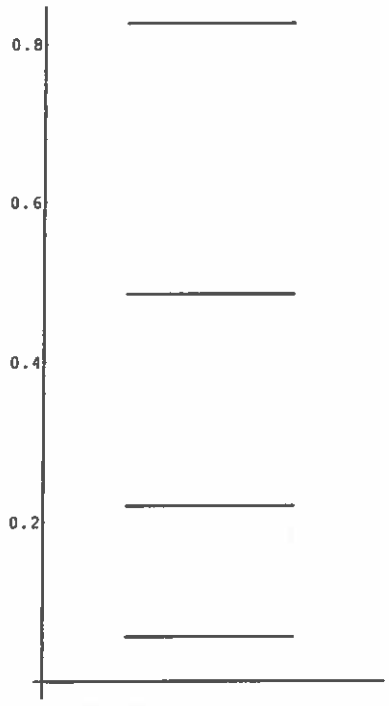
Out[19]:=

0.826332

There are just four *bound* states. We can make an energy level diagram by combining plots that draw lines at the appropriate energies. The **Plot[ ]** option, 'DisplayFunction → Identity', stops the actual display of the plot. Resetting 'DisplayFunction → $DisplayFunction' to its default assignment is required to turn displaying back on.

In[20]:=

```
Show[Plot[0,{x,0,2},DisplayFunction -> Identity],
Plot[e1,{x,0.5,1.5},DisplayFunction -> Identity],
Plot[e2,{x,0.5,1.5},DisplayFunction -> Identity],
Plot[e3,{x,0.5,1.5},DisplayFunction -> Identity],
Plot[e4,{x,0.5,1.5},DisplayFunction -> Identity],
AspectRatio -> 2,AxesOrigin -> {0,0},
Ticks -> {None,Automatic},DisplayFunction -> $DisplayFunction];
```



D=fferent states
D. fferent Energies

Out[20]:=

– Graphics –

We can find numerical values for the expansion coefficients by setting D=1 and then solving the first three equations in the original set for A, B, and C.

In[21]:=

```
v=m.{A,B,C,1}/.numbs
```

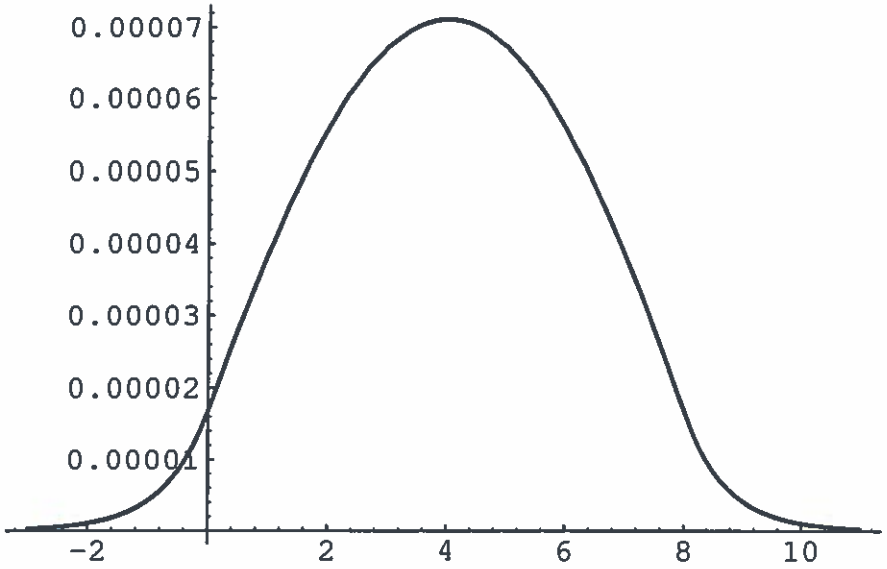
Out[21]:=

```
{A - C, A*(2 - 2*e)^(1/2) - 2^(1/2)*B*e^(1/2),
-E^(-8*(2 - 2*e)^(1/2)) + C*Cos[8*2^(1/2)*e^(1/2)] + B*Sin[8*2^(1/2)*e^(1/2)],
(2 - 2*e)^(1/2)/E^(8*(2 - 2*e)^(1/2)) + 2^(1/2)*B*e^(1/2)*Cos[8*2^(1/2)*e^(1/2)] -
2^(1/2)*C*e^(1/2)*Sin[8*2^(1/2)*e^(1/2)] }
```

In the following step we take the equations which fix A, B and C for the first eigenvalue, solve for A, B and C, generate functions that represent the solutions in the three regions, and (finally) plot the functions out.

In[22]:=

```
t=e1;
b=3;
vx=N[v/.e -> t];
soln=Solve[{vx[[1]]==0,vx[[2]]==0,vx[[3]]==0},{A,B,C}][[1]];
left=f1[x]/.numbs/.e -> t/.soln;
center=f2[x]/.numbs/.e -> t/.soln;
right=f3[x]/.numbs/.e -> t/.D -> 1;
Show[Plot[left,{x,-b,0},DisplayFunction -> Identity],
Plot[center,{x,0,L/.numbs},DisplayFunction -> Identity],
Plot[right,{x,L/.numbs,L+b/.numbs},DisplayFunction -> Identity],
DisplayFunction -> $DisplayFunction]
```

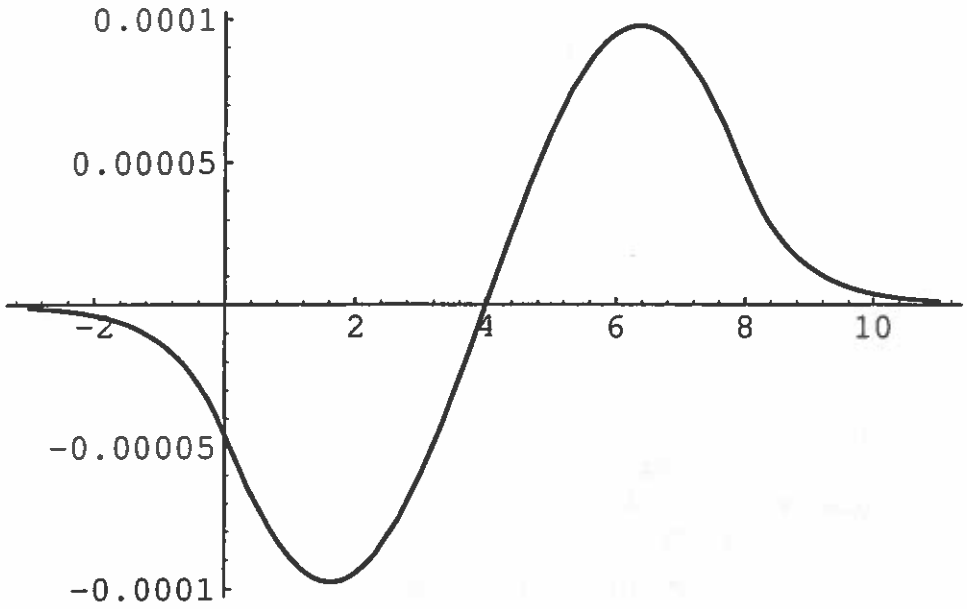


Out[22]:=

- Graphics -

In[23]:=

```
t=e2;
b=3;
vx=N[v/.e -> t];
soln=Solve[{vx[[1]]==0,vx[[2]]==0,vx[[3]]==0},{A,B,C}][[1]];
left=f1[x]/.numbs/.e -> t/.soln;
center=f2[x]/.numbs/.e -> t/.soln;
right=f3[x]/.numbs/.e -> t/.D -> 1;
Show[Plot[left,{x,-b,0},DisplayFunction -> Identity],
Plot[center,{x,0,L/.numbs},DisplayFunction -> Identity],
Plot[right,{x,L/.numbs,L+b/.numbs},DisplayFunction -> Identity],
DisplayFunction -> $DisplayFunction]
```



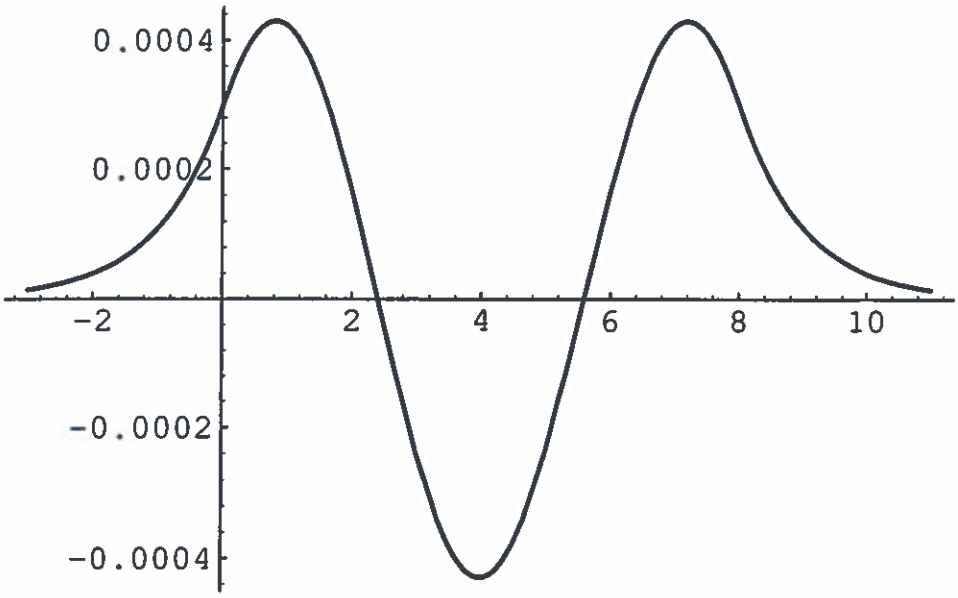
Out[23]:=

- Graphics -

In[24]:=

```
t=e3;
b=3;
vx=N[v/.e -> t];
soln=Solve[{vx[[1]]==0,vx[[2]]==0,vx[[3]]==0},{A,B,C}][[1]];
left=f1[x]/.numbs/.e -> t/.soln;
center=f2[x]/.numbs/.e -> t/.soln;
right=f3[x]/.numbs/.e -> t/.D -> 1;
Show[Plot[left,{x,-b,0},DisplayFunction -> Identity],
Plot[center,{x,0,L/.numbs},DisplayFunction -> Identity],
Plot[right,{x,L/.numbs,L+b/.numbs},DisplayFunction -> Identity],
```

```
DisplayFunction -> $DisplayFunction]
```

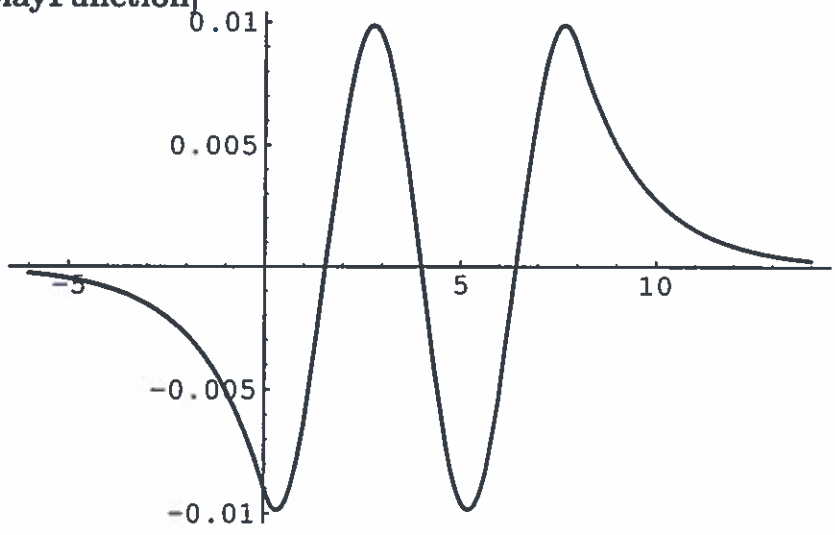


Out[24]:=

- Graphics -

In[25]:=

```
t=e4;
b=6;
vx=N[v/.e -> t];
soln=Solve[{vx[[1]]==0,vx[[2]]==0,vx[[3]]==0},{A,B,C}][[1]];
left=f1[x]/.numbs/.e -> t/.soln;
center=f2[x]/.numbs/.e -> t/.soln;
right=f3[x]/.numbs/.e -> t/.D -> 1;
Show[Plot[left,{x,-b,0},DisplayFunction -> Identity],
Plot[center,{x,0,L/.numbs},DisplayFunction -> Identity],
Plot[right,{x,L/.numbs,L+b/.numbs},DisplayFunction -> Identity],
DisplayFunction -> $DisplayFunction]
```



Out[25]:=

- Graphics -

Problem Set #1

1. What is the probability that an electron will be found *outside* a well?

Consider a well of length $L = 5.5$ and depth $V = 1$ (in atomic units). This system has three bound states. Determine the energies of these states. Make an energy level diagram for these states. Make a single plot that superimposes all three *normalized* eigenfunctions. [That is, bring two plots to class to hand in!]

You can integrate with In[ ] := Integrate[f[x],{x,-Infinity,0}], for example, and take a square root with In[ ] := Sqrt[...]

You will need these energy values and these state functions later. You can *save* these by copying the *results* of the present calculation into a new *Mathematica Notebook* that contains *explicit* definitions of these quantities:

You can create a function which is equal to $$\begin{cases} x^2 & \text{in } x \le 1, \\ 2-(x-2)^2 & \text{in } 1 \le x \le 3, \\ (x-4)^2 & \text{in } 3 < x \end{cases}$$ with three *conditional* statements: F[x_/; x <= 1]:= x^2 F[x_/; 1 < x <= 3]:= 2 − (x − 2)^2 F[x_/; 3 < x]:= (x − 4)^2

Calculate, for each of these states, the probability that the electron will be found outside $0 \le x \le 5.5$. Write in (by hand) the results on the level diagram!

2. As V is increased, the number of 'bound' states increases. At what values of V does the number of 'bound' states change? What is the precise relation between the number of 'bound' states and V?

3. As V is increased, the penetration distance outside the well is decreased. The solutions approach those of a 'particle in a box'. In the limit that $V \to \infty$, what are the boundary conditions, the energy eigenstates, and the energy eigenvalues? How does the energy level diagram compare with that of question 1? (Make a level diagram with *two* columns!)

Symmetry Transformation? always commute with $\hat{H}$

$\hat{S}\hat{H} = \hat{H}\hat{S}$ They commute

4. Consider the physical problem associated with the *double well*

$$V(x) = \begin{cases} 1, & \text{for } x < 0, \\ 0, & \text{for } 0 \le x \le 5.5, \\ 1, & \text{for } 5.5 < x < 6.5, \\ 0, & \text{for } 6.5 \le x \le 12, \\ 1, & \text{for } x > 12 \end{cases}$$

in atomic units. Make an energy level diagram showing the lowest 6 levels of this system. Comment on the relation of this level diagram to that corresponding to question 1.

Make a plot of the (normalized, superimposed) two lowest eigenfunctions and a similar plot of the next two levels. On the basis of these plots suggest an approximate representation for the states of a double well system. Prepare a plot which allows one to judge the quality of the approximation.